

# Statistical Thermodynamics in Chemistry and Biology

## 24. Intermolecular interactions

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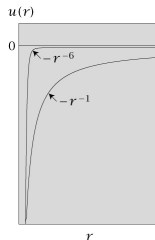
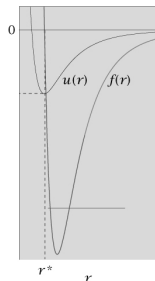
# Intermolecular interactions

## This chapter:

- ▶ Brief background of intermolecular interactions
- ▶ Foundation for more complex statistical thermodynamical models with more accurate models for the interaction between particles.

# Typical potential surfaces

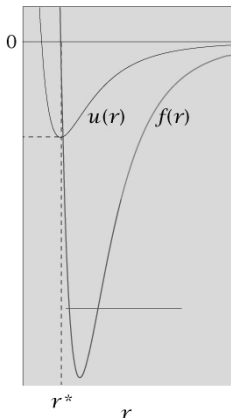
- ▶ Intermolecular interaction energies are 0 at long distances (definition/convention).
- ▶ Molecules normally (but not always) attract each other at intermediate distances.
- ▶ Molecules always repel each other at short distances.
- ▶ Coulomb's law behave as  $r^{-1}$  and is the most long-range interaction.
- ▶  $r^{-6}$  is a typical distance-dependence of a short-range interaction.



## Example: Argon dimer

- ▶ An argon atom is spherically symmetric (no dipole moment) and uncharged.
- ▶ At intermediate range they attract each other because of **London dispersion forces**. Dispersion energies can be derived from quantum mechanics, and arises from fluctuations in the charge distribution (fluctuation dipole moments).
- ▶ At short range, the atoms repel each other because of the **Pauli exclusion principle**, i.e. two electrons cannot be in the same quantum-mechanical state.
- ▶ The sum of these two terms are normally termed **van der Waals** interactions, and are normally modelled with a **Lennard-Jones** potential,

$$V_{\text{LJ}} = \sum_{i,j>i} \left( \frac{a_{ij}}{r_{ij}^{12}} - \frac{c_{ij}}{r_{ij}^6} \right)$$

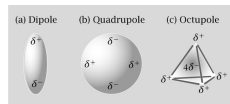


# Electrostatic interactions

- ▶ For charged and polar molecules, the electrostatic interactions **dominate**. Coulomb's law,

$$V_{\text{Coul}} = \sum_{i,j>i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

- ▶ Molecules are characterized by the leading non-zero electric moment: monopole (charge), dipole moment, quadrupole moment, octupole moment, etc.
- ▶ The electrostatics is often represented by **atomic charges** that gives the correct molecular electric moments.
- ▶ Electrostatic interactions can be either attractive or repulsive (for example depending on the orientation of the dipole moment), which **often** determines if the overall interaction energy is attractive or repulsive.



# Electrostatic interactions

## Part 2

- ▶ For dipole-dipole interactions to be attractive in the condensed phase, it often leads to an ordering of the system (which decreases the entropy).
- ▶ Distance-dependence of electrostatic interactions:
  - ▶ charge-charge:  $r^{-1}$
  - ▶ charge-dipole:  $r^{-2}$
  - ▶ charge-quadrupole and dipole-dipole:  $r^{-3}$
  - ▶ charge-octupole and dipole-quadrupole:  $r^{-4}$
  - ▶ etc.
- ▶ Still more long-range than dispersion interactions ( $r^{-6}$ ).

# Polarization energies

Not good in the book. Polarization and dispersion are confused with each other

- ▶ We make a distinction between permanent dipole moments (include in the electrostatic term) and **induced dipole moments** (included in the polarization energy).
- ▶ An induced dipole moment arises from that the electrons are polarized (shifted away from the nuclei) in an electric field.
- ▶ The induced dipole moment,  $\vec{\mu}_{\text{ind}}$ , is given as

$$\vec{\mu}_{\text{ind}} = \alpha \vec{E}$$

where  $\alpha$  is a **polarizability** and  $\vec{E}$  is the electric field.

- ▶ The electric field arises from external sources, the molecular electric moments of the other molecules, and from the induced dipole moments of the other molecules (leads to a set of coupled equations)
- ▶ Electronic polarization gives an extra energy contribution that is always attractive (the molecules polarize in such a way that the total energy is lowered).

# An example

## The interaction between an Ar atom and an ion

- ▶ Is the leading interaction energy between an Ar atom and an ion a dispersion energy or a polarization energy?
- ▶ It is a polarization energy. The argument is as follows.
- ▶ The ion with charge  $q$ , gives an electric field at the Ar atom,

$$\vec{E} = -\vec{\nabla} \left( \frac{q}{R} \right)$$

where the electric field is minus the gradient of the electrostatic potential.

- ▶ The Ar atom is polarized by the field and gets an induced dipole moment,  $\vec{\mu}^{\text{ind}}$ ,

$$\vec{\mu}^{\text{ind}} = \alpha \vec{E}$$

- ▶ The induced dipole moment interacts with the charge according to electrostatics (formula for the polarization energy is not derived),

$$V = -\frac{1}{2} \sum_I \vec{\mu}_I^{\text{ind}} \cdot \vec{E}_I = -\frac{1}{2} \sum_I \alpha_I \vec{E}_I \cdot \vec{E}_I$$

- ▶ In the literature, often regarded as a van der Waals term...



# Hydrogen bonds

- ▶ Hydrogen bonds are crucial in many systems (aqueous solutions, proteins, etc.) but are difficult to model accurately.
- ▶ Example:  $\text{N-H} \cdots \text{O}=\text{C}$
- ▶ The interaction is strongly orientation-dependent and increases the “structure” of the system.
- ▶ To a good degree, the hydrogen bond is described by electrostatics and may be modelled by **local dipole moments**.

# Force fields - empirical energy functions

- ▶ In addition to van der Waals, electrostatic and polarization contribution, a **force field** contains terms to model intramolecular energies:
  - ▶ Bond stretches (by a harmonic term),

$$\frac{k_b}{2} (b - b_0)^2$$

- ▶ Bond angles (also by a harmonic term)

$$\frac{k_\theta}{2} (\theta - \theta_0)^2$$

- ▶ Dihedral angles (by a periodic term)

$$k_\phi (1 + \cos(n\phi - \delta))$$

where  $k_b$ ,  $k_\theta$  and  $k_\phi$  are force-field parameters.

# The van der Waals gas model

- ▶ The van der Waals gas model is an extension of the ideal gas law that includes some interatomic interactions.
- ▶ The **van der Waals equation of state**,

$$p = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2} = \frac{\rho RT}{1 - b\rho} - a\rho^2$$

where  $a$  and  $b$  are parameter, both larger than zero.

- ▶ The  $b$  parameter gives a “volume” for each particle.
- ▶ The  $a$  parameter includes an attractive interaction between the gas molecules.
- ▶ A derivation using “our machinery” is given in E24.2 (only in part the same as the derivation in the book on pages 480-482).

# Summary

- ▶ Introduction to intermolecular forces
- ▶ Basically four contributions:
  - ▶ Dispersion and repulsion (grouped as van der Waals interactions)
  - ▶ Electrostatics (most important for charged or polar systems)
  - ▶ Polarization energies
- ▶ Introduction to equation of states with the van der Waals gas model as an example

## E24.3 (Exam Aug. 2012:3)

a) In our models, we normally use an interaction parameter  $w_{XY}$  to describe intermolecular interactions. For more sophisticated models of intermolecular interactions, the interaction energy is often partitioned into four terms: electrostatic energy, polarization energy, repulsion energy, and dispersion energy. Discuss the physical origin of each energy term, and discuss the relative distance-dependence of each term (e.g. which terms are most important at long distances between the molecules?).

b) Compare liquid argon and liquid water. Which energy terms in a) would be most important for respective liquid at long distances? Discuss the relative importance of each energy term for the two cases.

## E24.2

Derive the van der Waals' equation of state in eq. 24.15

$$p = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

by using a lattice model. Derive expressions for the  $a$  and  $b$  parameters. Are  $a$  and  $b$  positive or negative numbers (motivate the answer)? The Bragg-Williams approximation should be used for the energy term. For the entropy term, extend Example 6.1 with one more term in eq. 6.12 as well as make use of the approximation valid for small  $x$

$$1 + \frac{x}{2} \approx \frac{1}{1 - \frac{x}{2}}$$